Formation of $Ni[C_4(CN)_8]$ from the reaction of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) with TCNE in THF

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The dissolution of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) into dichloromethane leads to decomposition and formation of a room temperature magnetic material, whereas the reaction of $Ni(COD)_2$ and tetracyanoethylene (TCNE) in THF forms paramagnetic materials including $Ni^{II}[C_4(CN)_8](THF)_2 \cdot x$THF. These results are discussed in context with a recent report of a room temperature magnet based upon the reaction of $Ni(COD)_2$ and TCNE in dichloromethane.

Introduction

Since the report of the first organic-based magnet, $[Fe(C_5Me_5)_2]^{\bullet+}[TCNE]^{\bullet-}$ (TCNE = tetracyanoethylene),[1,2] several other families of $[TCNE]^{\bullet-}$-based magnets have been reported. These include $M[TCNE]_x \cdot zCH_2Cl_2$ {$x \sim 2$; $z \sim 0.5$; M = V,[3] Mn,[4,5] Fe,[4,6] Co,[4,7] Ni,[4,8]}, [MnTPP][TCNE]·z(solvent) (H_2TPP = *meso*-tetraphenylporphyrin),[9] and recently $[Fe^{II}(TCNE)(NCMe)_2][Fe^{III}Cl_4]$ with a 2 : 1 Fe : TCNE ratio.[10] The highest T_c observed is 400 K (127 °C) for $V[TCNE]_x \cdot zCH_2Cl_2$; however, these materials exhibit degraded T_cs upon heating above ~350 K and/or exposure to air.

Recently Hicks and co-workers reported a major enhancement with respect to the air stability as well as a higher T_c for a Ni(II)–$[TCNE]^{\bullet-}$-based magnet.[11] These authors claim that reaction of bis(1,5-cyclooctadiene)nickel(0), $Ni(COD)_2$, with TCNE, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) dissolved in dichloromethane, and after exposure to air, forms an 'ill-defined' metal–organic magnet of, for example, $Ni_2(TCNE)O(OH)(OH_2)_2(CH_2Cl_2)_{1/8}$ composition that magnetically orders above room temperature.

Results and discussion

While $Ni(COD)_2$[12] is known to decompose in air,[13a] even within an inert atmosphere glove box (<0.5 ppm O_2 and H_2O), $Ni(COD)_2$ immediately decomposes upon dissolution into dichloromethane to form a black powder, and a resultant colorless solution possessing 1,5-cyclooctadiene. This black powder is immediately attracted to a magnetic stirring bar (Fig. 1). Formation of colloidal Ni has been reported from the reaction of $Ni(COD)_2$ and dichloromethane in the presence of polyvinylpyrrolidone (which is used to control the particle size).[13c,d] The temperature dependent magnetization, $M(T)$, of this black powder (Fig. 2) is comparable to that reported in Fig. 1 of reference 11, as well as Fig. 3 in reference 13(*d*) for colloidal Ni made from $Ni(COD)_2$.

Fig. 1 Black powder reaction product, which forms when $Ni(COD)_2$ is dissolved in dichloromethane, is attracted to a magnet. Photograph by William W. Shum.

$Ni(COD)_2$ is inherently unstable[13a] and autocatalytically decomposes in the presence of Ni(0).[13b] Even in the solid state bright-yellow $Ni(COD)_2$ stored in a freezer exhibits slow decomposition (as we note the presence of ~200 and ~700 ppm Ni^0,[14]

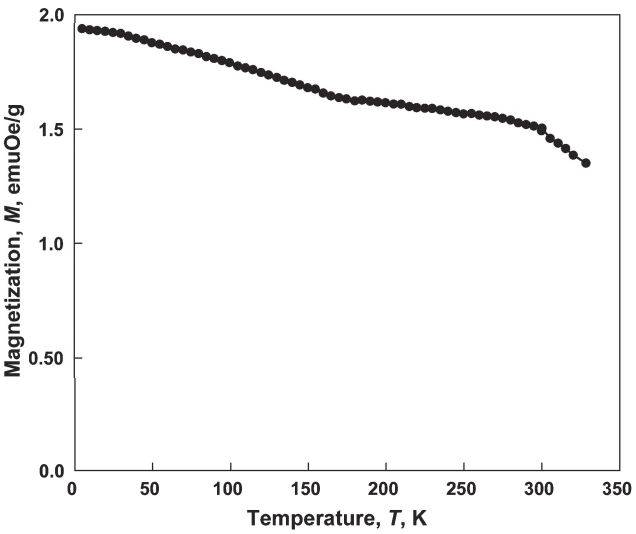

Fig. 2 $M(T)$ for black particles formed from $Ni(COD)_2$ dissolved in dichloromethane.

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respectively, for different sources). Note that these $Ni^0(COD)_2$ samples appear to be pure to the eye—even in solution—as upon dissolution in THF or toluene they immediately give a transparent yellow solution. However, light from a HeNe laser does exhibit light scattering (Tyndall effect) suggesting a colloidal character of the solutions due to Ni particles comparable in size to the 633 nm wavelength of the light. Additionally, upon longer standing in either THF or toluene at room temperature within a glove box, decomposition forming a Ni mirror occurs.

Reaction of TCNE and $Ni(COD)_2$ in THF in a 2 : 1 ratio forms a green product exhibiting ν_{CN} 2238 and 2187 cm^{-1} absorptions (Fig. 3). Based upon the elemental analysis this material is formulated as $Ni(TCNE)_2{\cdot}3.45THF$.[15] Similar ν_{CN} absorptions at 2242 and 2191 cm^{-1} were observed for the green product of the reaction of $[Ni^{II}(NCMe)_6]^{2+}$ [16] and $[TCNE]^{\bullet -}$ in MeCN. Related reactions involving $[M^{II}(NCMe)_6]^{2+}$ (M = Mn, Fe) yield $M[C_4(CN)_8](NCMe)_2{\cdot}S$ (S = solvent) with ν_{CN} peaks at 2205 and 2153 cm^{-1} and at 2213 and 2154 cm^{-1}, respectively.[17] The ~30 cm^{-1} blue shift is consistent with that observed in $[M^{II}(NCMe)_6][SbF_6]_2$ (M = Mn, Fe, Co, Ni) when either Mn or Fe is replaced by Ni.[16] Thus, this compound formed *via* the 2 : 1 TCNE : Ni ratio is formulated as $Ni[C_4(CN)_8](THF)_2{\cdot}1.45(THF)$, and possesses μ_4-$[C_4(CN)_8]^{2-}$.

The observed ν_{CN} absorptions, however, may also be due to the presence of μ_4-$[TCNE]^{\bullet -}$ as observed for $[Fe(TCNE)(NCMe)_2][FeCl_4]$ (*i.e.* 2222 and 2178 cm^{-1}),[10] or both μ_4-$[TCNE]^{\bullet -}$ and μ_4-$[C_4(CN)_8]^{2-}$ as reported for $Fe[TCNE][C_4(CN)_8]_{1/2}{\cdot}z(CH_2Cl_2)$ (*i.e.* 2221 and 2172 cm^{-1}).[18] The observed frequencies are 15 ± 5 cm^{-1} higher than those of $Ni[TCNE]_2{\cdot}zCH_2Cl_2$ prepared from TCNE and $Ni(CO)_4$ (*i.e.* 2218 and 2178 cm^{-1}),[8] but nominally comparable to this material prepared from $NiI_2{\cdot}z$MeCN and TCNE (*i.e.* 2237 and 2194 cm^{-1}).[4]

In contrast, the reaction of TCNE and $Ni(COD)_2$ in THF in a 1 : 2 ratio forms a brown product exhibiting ν_{CN} absorptions at 2201 and 2116 cm^{-1} (Fig. 3).[19] Analysis of the elemental composition as well as the color suggest that this product is a mixture of more than one component, which includes some $Ni(TCNE)_2{\cdot}x$THF as well as perhaps μ_4-$[TCNE]^{2-}$ based upon the low energy ν_{CN} absorption.

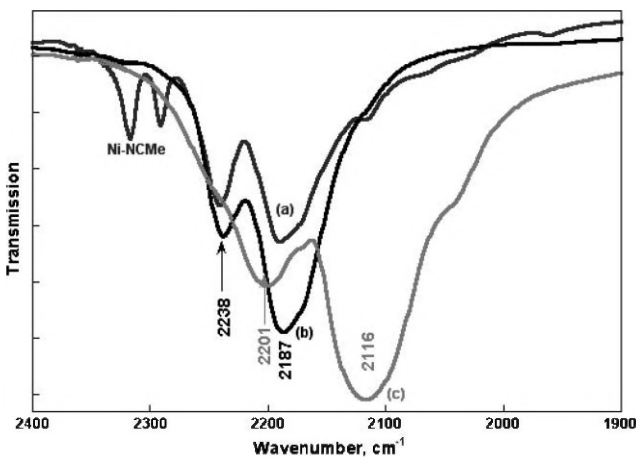

Fig. 3 The ν_{CN} region of the IR spectra of the reaction products of TCNE and $Ni(COD)_2$ in THF in 1 : 2 (b) and 2 : 1 (c) ratios. The spectrum of $Ni[C_4(CN)_8](NCMe)_2$ (a) is shown for comparison.

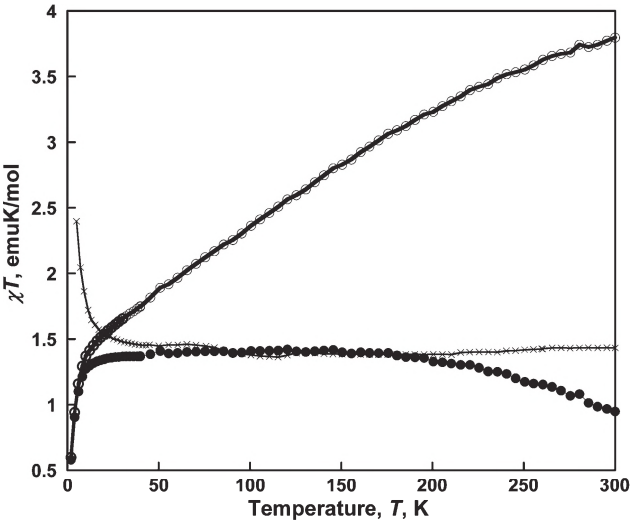

Fig. 4 $\chi T(T)$ for $Ni[C_4(CN)_8](THF)_2{\cdot}1.45(THF)$ (○) that includes a temperature independent contribution of ~300 ppm of Ni (●). $\chi T(T)$ for $Ni[C_4(CN)_8](NCMe)_2{\cdot}$MeCN (×) is shown for comparison.

The 5 to 300 K temperature dependent magnetic susceptibility, χ, of $Ni(TCNE)_2{\cdot}3.45THF$ is reported as $\chi T(T)$, Fig. 4. Above 15 K $\chi T(T)$ increases almost linearly suggesting a substantial temperature independent component, most probably ferromagnetic in origin. As noted above, $Ni(COD)_2$ slowly decomposes at room temperature in THF solution, and more than 200 ppm of ferromagnetic Ni^0 impurities are expected. The susceptibility of nanosize Ni^0 particles are temperature dependent, especially when approaching critical temperature.[20] This temperature independent component corresponds to ~300 ppm Ni, and upon correcting the $\chi T(T)$ data, $\chi T(T)$ is temperature independent in the $10 < T <$ 170 K region. Above 170 K $\chi T(T)$ decreases as a consequence of the temperature dependence of the ferromagnetic contribution. The χT value at 170 K for $Ni(TCNE)_2{\cdot}3.45THF$ is 1.41 emu K mol^{-1}, which is typical for high-spin Ni(II) ions ($S = 1$, $g = 2.37$).[21] This is in accord with the presence of diamagnetic $[C_4(CN)_8]^{2-}$ in agreement with the IR spectra. The drop in $\chi T(T)$ below 10 K is most probably due to a weak antiferromagnetic coupling between Ni(II) ions.

The product of the reaction of TCNE and $Ni(COD)_2$ in a 1 : 2 ratio reaction also exhibits a susceptibility composed of a paramagnetic component and a temperature independent component (below 200 K) attributed to the Ni^0 present from the starting $Ni(COD)_2$ material. It does not order magnetically, and its multiphase composition makes the detailed analysis inconclusive.

Furthermore, the presence of reduced TCNE, as claimed in reference 11, is quite unlikely since the reduced radical anion of TCNE, $[TCNE]^{\bullet -}$, very quickly reacts with water/oxygen to form $[C_2(CN)_3O]^-$ and other species[22] that unlike $[TCNE]^{\bullet -}$ do not enable magnetic ordering.[23] The $[C_2(CN)_3O]^-$ species has diagnostic infrared absorptions at ~2225 ± 20 (ν_{CN}), ~2197 ± 17 (ν_{CN}), and ~1585 ± 35 cm^{-1} (ν_{CO}),[23,24] which appear to be consistent with spectra reported as supplementary Fig. 2c of reference 11. Metal complexes of $[C_2(CN)_3O]^-$ are typically unintentionally made and are isolated from the hydrolysis of either TCNE or $[TCNE]^{\bullet -}$, and their presence has surprised several research groups.[23,24] Similarly, related $[TCNQ]^{\bullet -}$ and

$[C_4(CN)_6]^{\bullet-}$ have been reported to undergo this hydrolysis to form diamagnetic $[(NC)_2C_6H_4C(O)CN]^-$ [25a] and $[C_4(CN)_5O]^-$,[25b] respectively.

Conclusion

Presumably the magnetic material made upon dissolution of $Ni(COD)_2$ in CH_2Cl_2 consists of 'nano'- or greater-sized particles of nickel metal. This black powder magnetic material may also have chlorine, carbon, and/or hydrogen present, but it certainly lacks the organic species used in the aforementioned paper. The identification of the magnetically active component of organic- and molecule-based magnets remains challenging,[26] as several reports have failed to stand the test of time[27–29] in spite of publicity they have garnered.

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